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15. SUBJECT TERMS

Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. 239.18

Taming Hazardous Reactive Materials for Single Crystal X-ray Diffraction Studies: Dealing with Handling and Disorder Nightmares



July 9, 2004 University of Bialystok Bialowicia, Poland

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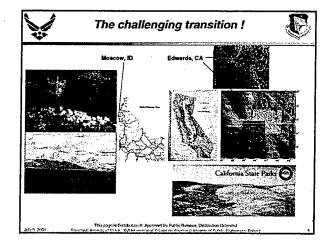
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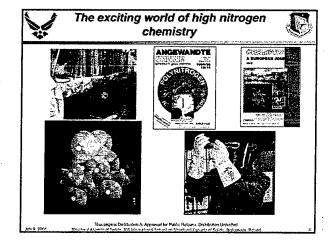
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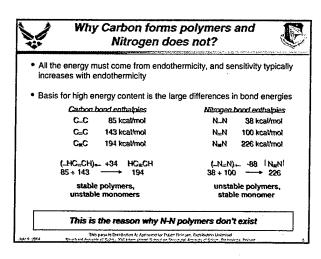
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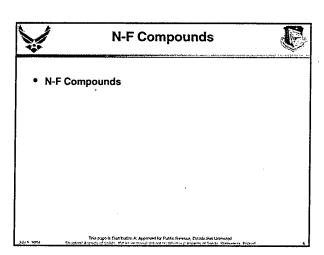
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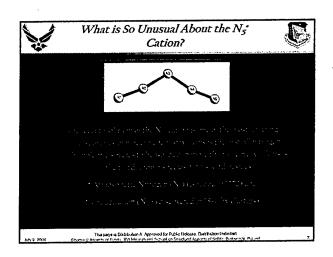
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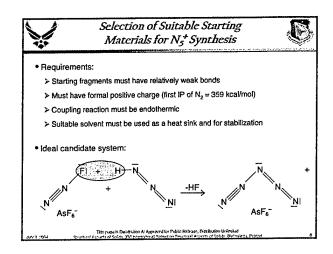


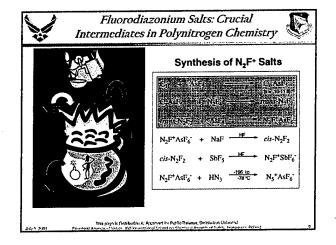


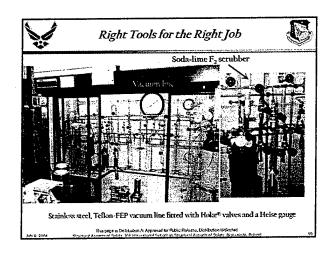


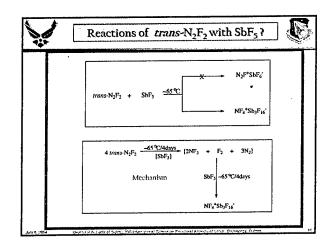


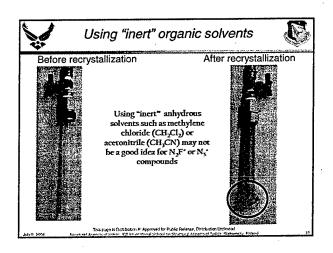














Recrystallization



- > HF is used as a solvent in most of the cases. It can be removed from the reaction product at low temperature: useful for thermally unstable compounds.
- > SO2 can also be used, if there are no compatibility issues. Sometimes complexation can be observed, i.e. Cs azide
- Mixtures of SO2 and SO2CIF can be used to alter solubility, i.e. N5+ is very soluble in SO2 but not much soluble in SO2CIF. SO2 b.p. =; SO2CIF (b.p. =). SO2 evaporates first resulting in reduced solubility



Mounting using LT apparatus



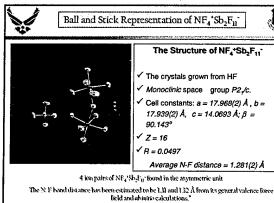
- > Specially designed dewar vessel where crystals are loaded into a glass lip under a clod nitrogen gas flow. The mounting is then accomplished using PFPE oil and Cryoloops.
- Useful for thermally unstable material, and compounds which are liquids at room temperature.



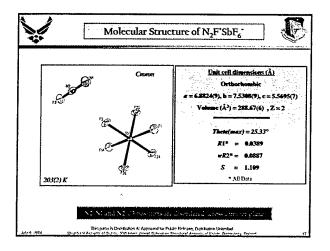
Hungry for cryoloops?

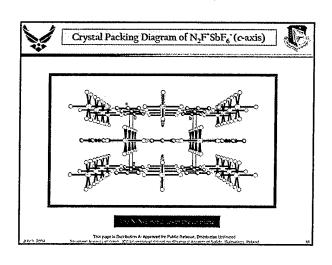


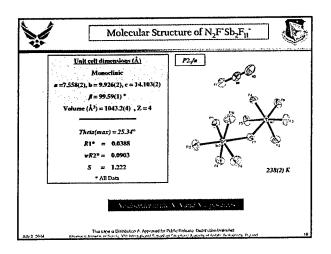
Contact from the oxidizer can chew up the cryoloop. In this case, the crystal can be embalmed in Kel-F grease to protect the Cryoloop. The crystal needs to be transported on the pre-centered goniometer head using a magnetic mount.

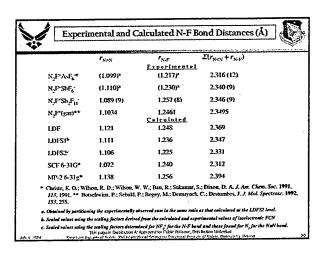


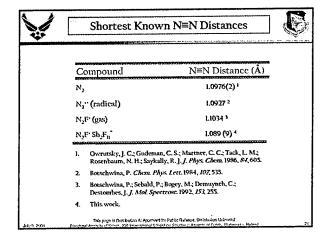
* Christe, K. O. Spectrochim. Acta, Part A 1986, 42A, 939 and references therein.

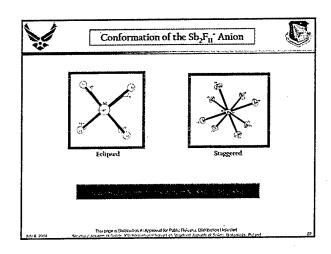


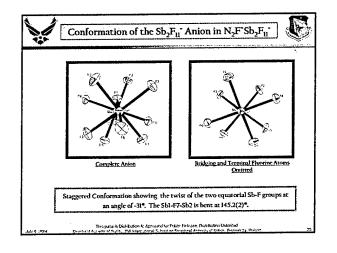


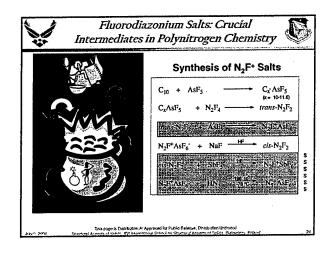














Actual Synthesis of N5+AsF6



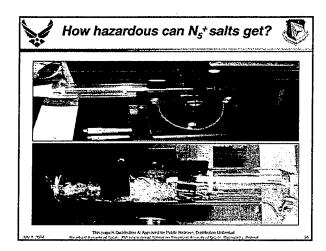
· Reaction system worked as planned:

$$N_2F^+AsF_6^- + HN_3 \xrightarrow{} N_5^+AsF_6^- + HF$$
 $^+78^\circC$

- ➤ High yield
- > Only byproducts were 20-40% H₂N₃+AsF₆⁻⁻
- > 2 mmol (0.5 g) scale
- Properties of N₅⁺AsF₆⁻:
 - ➤ White solid
 - > Sparingly soluble in HF
- ➤ Marginally stable at 22°C
- > Highly energetic
- > Reacts violently with water and organics
- ightharpoonup Calculated ΔH_{I} (298°C) = 351 kcal/mol

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The Taming of $N_5^+SbF_6^-$



- Desired a more stable N_s+ salt
- Prepared N₅*SbF₆-:

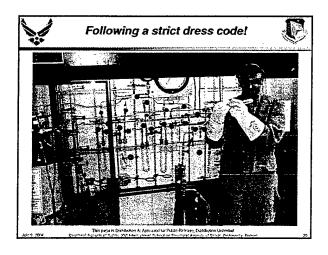
$$HF$$
 $N_2F^*SbF_6^- + HN_3 \longrightarrow N_5^*SbF_6^- + HF$
 $-78^{\circ}C \text{ to RT}$

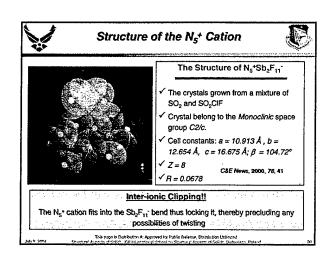
- Properties of N₅+SbF₆-:
- > White solid
- ➤ Stable to 70°C
- > Obtained in high purity
- > Does not explode at 150 kg-cm (impact sensitivity test)
- > Exhibits all the still missing vibrational bands with the predicted frequencies
- > Soluble in SO2, SO2CiF, and HF

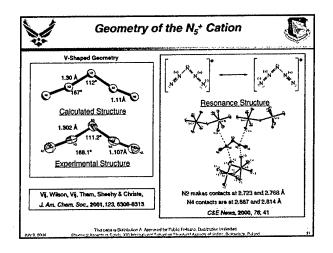
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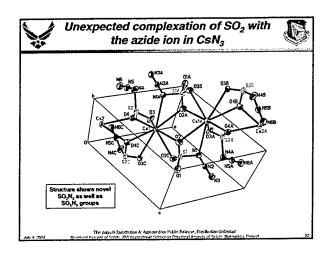
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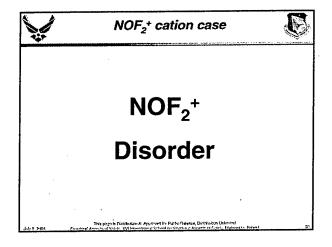


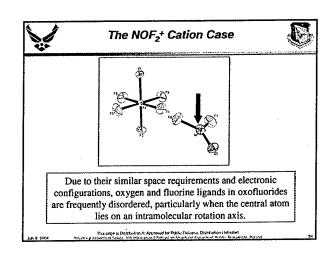


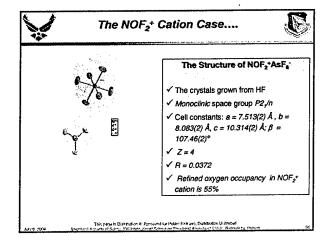


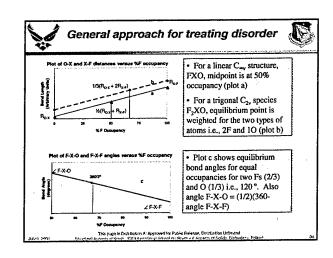


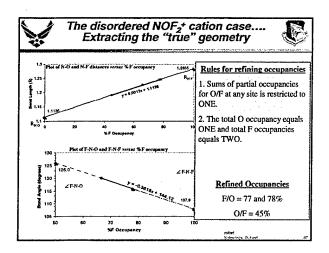


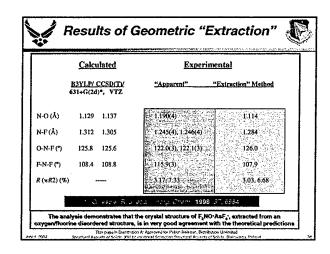


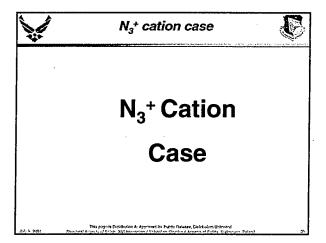


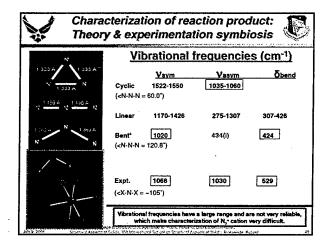


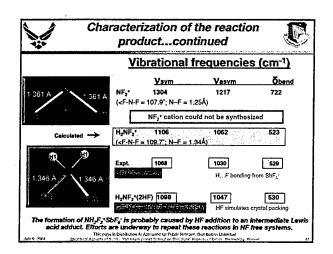


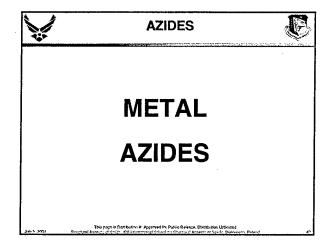


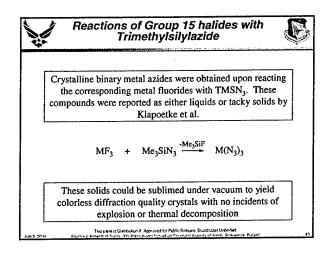


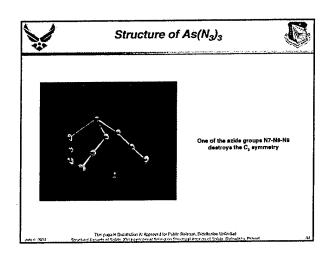


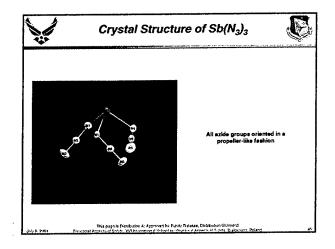


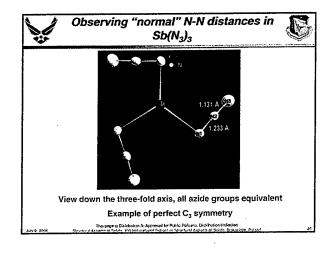


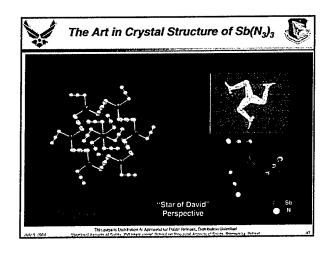


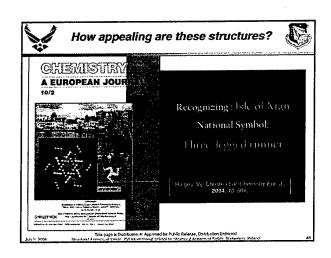


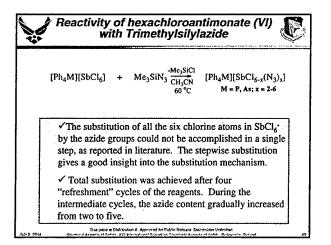


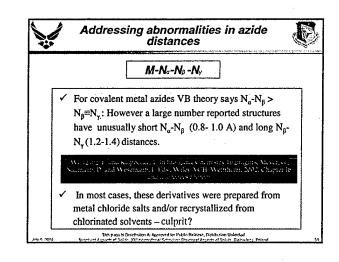


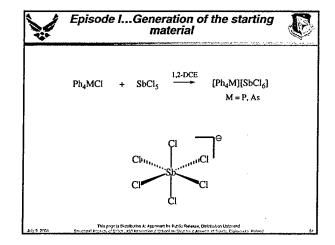


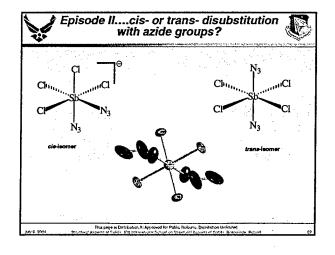


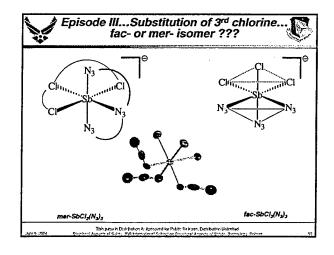


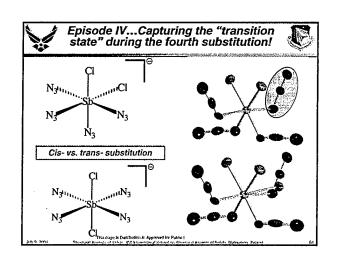


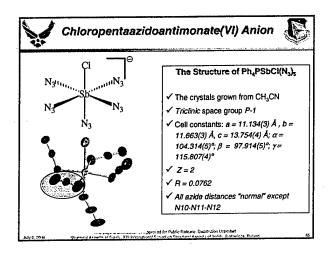


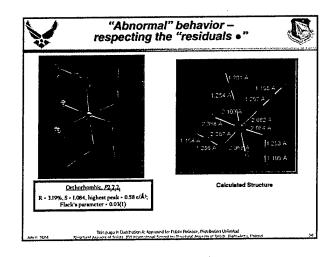


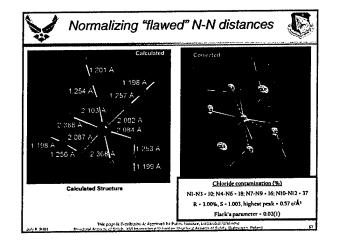


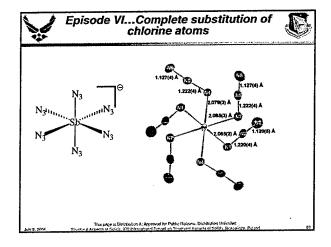


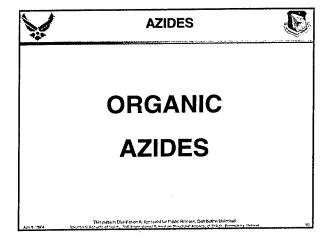


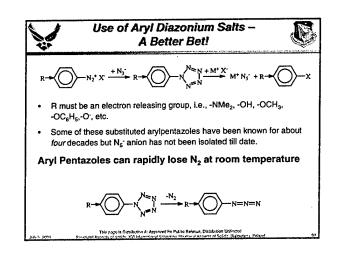


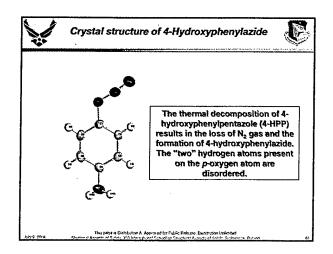


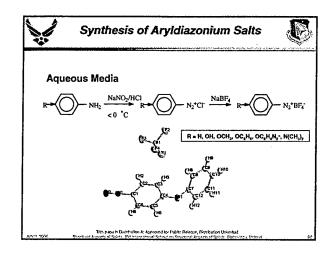


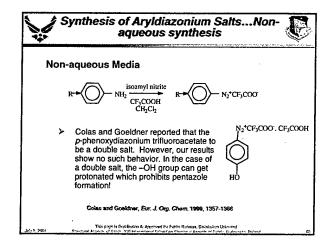


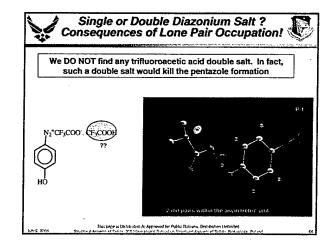


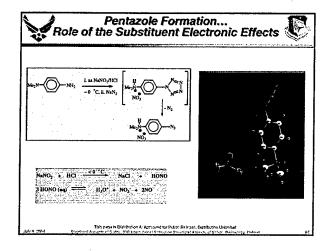


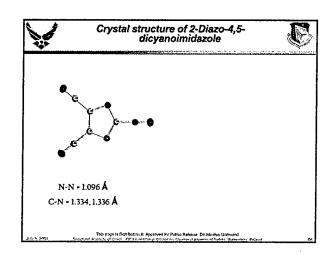


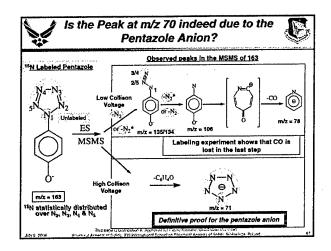


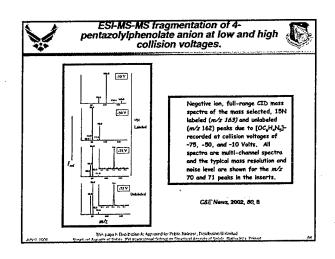


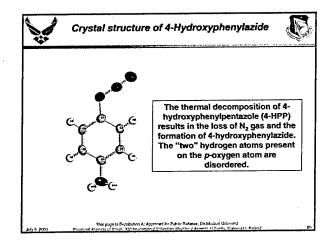


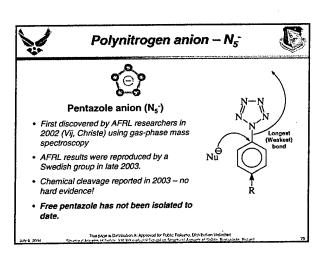


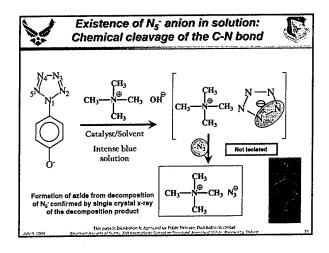


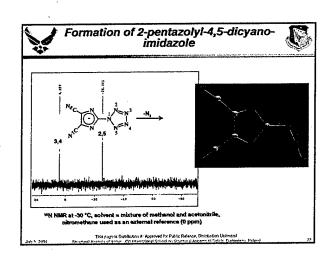














Summary Highlights



- ✓ The first ordered crystal structure of an N₂F' salt, thus providing individual N≡N and N-F bond lengths. N₂F'Sb₂F₀* compound contains the shortest known N≡N bond, which is shorter than that of N₂.
- The low temperature and safe preparation of NF₄* polyantimonates without the use of fluorine gas and high temperature/pressure. A non-disordered NF₄* anion is structurally characterized.
- ✓ The unique preparation of the N₂F₁ cation by the disproportionation of N₂F salts. The disorder has not been resolved yet!
- Solving the bond distance anomaly in the structure of NOF₂ cation by site occupancy refinement technique.
- Crystal structure of N₃* cation to prove the skeptics wrong on the existance of this exotic species.

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Conclusions



- AIF₃ is the best catalyst for the isomerization of trans-N₂F₂
- N₅* cation can be stabilized with anions such as B(CF₃)₄-, SnF₅-, SnF₆²-, SbF₆- and Sb₂F₁₁²- but <u>NOT</u> with N₃-, NO₃-, ClO₄- and N(NO₋)-
- Only one fluorine atom in N(O)F₂⁺ has been replaced with an azide ion to form the N₃N(O)F⁺ cation
- > The N₂(N₃)₃+ cation could not be stabilized and isolated
- > The N(N₃)₄+ cation could not be stabilized and isolated
- Pentazoles with substituents other than the anyl group can be prepared and stabilized at low temperatures.
- 2-Pentazolyl-4,5-imidazole appears to undergo chemical C-N bond cleavage. Results are under investigation!

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